

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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## PCT

### NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(PCT Rule 71.1)

Date of mailing  
(day/month/year) 10.02.2006

Applicant's or agent's file reference  
P27136PC00/RKIMHO

#### IMPORTANT NOTIFICATION

International application No.  
PCT/NL2004/000051

International filing date (day/month/year)  
21.01.2004

Priority date (day/month/year)  
21.01.2004

Applicant  
AVANTIUM INTERNATIONAL B.V. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international  
preliminary examining authority:



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# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P27136PC00/RKIMHO		<b>FOR FURTHER ACTION</b>		See Form PCT/PEA418
International application No. PCT/NL2004/000051		International filing date ( <i>day/month/year</i> ) 21.01.2004		Priority date ( <i>day/month/year</i> ) 21.01.2004
International Patent Classification (IPC) or national classification and IPC B01J23/72, B01J37/08, C07C29/154, B01J23/745, B01J23/89				
Applicant AVANTIUM INTERNATIONAL B.V. et al.				
<p>1 This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2 This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3 This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of 4 sheets, as follows:</p> <p><input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand  21.11.2005		Date of completion of this report  10.02.2006		
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer  Jourdan, A  Telephone No +49 89 2399-8349 		

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

10/587108  
AP2003/000051  
21 JUL 2006  
International application No.  
PCT/NL2004/000051

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-24 as originally filed

**Claims, Numbers**

1-32 received on 21.11 2005 with letter of 21.11.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing *(specify):*
  - ☐ any table(s) related to sequence listing *(specify):*
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing *(specify):*
  - ☐ any table(s) related to sequence listing *(specify):*

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/NL2004/000051

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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**1. Statement**

Novelty (N)	Yes: Claims	1-32
	No: Claims	
Inventive step (IS)	Yes: Claims	1-32
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-32
	No: Claims	

**2. Citations and explanations (Rule 70.7):**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(SEPARATE SHEET)**

44/587108  
AP2003/000001 21 JUL 2006  
International application No.

PCT/NL2004/000051

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

Reference is made to the following documents:

D1: US-A-4 279 781 (DIENES EDWARD K ET AL) 21 July 1981 (1981-07-21)

D2: US-A-4 876 402 (MERRIAM JAY S ET AL) 24 October 1989 (1989-10-24)

Document D1 discloses a catalyst for the methanol synthesis. The catalyst is derived by in situ reduction from a catalyst precursor comprising copper oxide and zinc oxide carried on a thermal stabilizing metal oxide such as aluminium oxide. The catalyst precursor can be prepared by contacting a mixed solution of copper ammine carbonate complex and zinc ammine carbonate complex with the thermal stabilizing metal oxide, thermal decomposition of the complexes into basic zinc carbonates and subsequent calcination thereof.

Document D2 discloses a reduced catalyst precursor comprising copper oxide and zinc oxide impregnated with a selectivity enhancer such as alkali metal, nickel or cobalt. The catalyst may be supported on e.g. on silica, alumina, zirconia etc. The catalyst precursor may be prepared by the thermal decomposition of an aqueous mixture of copper and zinc ammine complexes into the corresponding carbonates in the presence of a thermally stabilizing carrier such as hydrated alumina. After the coprecipitation of the water-insoluble basic carbonates onto the carrier they are converted into oxides. (See passages cited in the international search report)

The subject-matter of claim 1 differs from D1 and D2 in that the final solution/carrier combination which is to be calcined comprises ions of an organic complexing agent. Hence, no intermediate precipitate is formed on the carrier. In comparative example 1 of the present application it is shown that a catalyst obtained by precipitating copper and iron in the presence of a carrier and then calcining the precipitate/carrier is worse in catalytic activity and selectivity in the hydrogenation of methyl laurate. Therefore it is credible that the catalyst claimed in claims 22-31 differs from those of D1 and D2.

**INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(SEPARATE SHEET)**

International application No.

PCT/NL2004/000051

None of the documents D6 and D9 disclose supported catalysts comprising copper and a second metal used for the hydrogenation of fatty acids, fatty esters which have been prepared starting from organic complex compounds. Therefore for the same reason as explained for the catalyst according to claims 22-31, the subject-matter of claim 32 seems to be novel.

The problem to be solved by the present invention is to improve the selectivity and/or activity in the catalytic hydrogenation of fatty acids and/or fatty esters. With regard to table 1 an improvement compared to catalysts prepared from supported precipitate precursors may be acknowledged.

21.11.2005

AP2003030740 21 JUL 2006

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PCT/NL2004/00051  
21-11-2005

(105)

C L A I M S

1. Method for the preparation of a chromium-free catalyst comprising Cu and at least one second metal in metallic or oxidic form, comprising the steps of:
  - 5 a) preparing a final solution comprising ions of Cu and of at least one second metal, said final solution additionally comprising ions of an organic complexing agent and having a pH of above 5;
  - b) contacting said final solution with inert carrier to form a final solution/carrier combination;
  - 10 c) optionally, drying the final solution/carrier combination;
  - d) calcining the final solution/carrier combination obtained in step c) or d) to yield Cu and the at least one second metal in oxidic form; and
  - 15 e) reducing at least part of the thus obtained oxidic Cu on the carrier.
2. Method according to claim 1, wherein the organic complexing agent is chosen from citric acid, lactic acid, and EDTA.
- 20 3. Method according to any of claims 1 or 2, step a) comprising the step of preparing said final solution by combining at least a first solution comprising ions of Cu with at least a second solution comprising ions of at least one second metal.
- 25 4. Method according to claim 3, wherein the first and second solutions both comprise ions of the complexing agent in a similar concentration.
- 30 5. Method according to any of claims 3 or 4, wherein both the first solution and the second solution have a pH of above 5.
6. Method according to claim 5, wherein the first and the second solution have a similar pH.

7. Method according to any of the preceding claims, wherein said chromium-free catalyst further comprises at least one third metal.
- 5 8. Method according to any of the preceding claims, wherein the pH of the final solution is above 6.
9. Method according to any of the preceding claims, wherein the concentration of Cu ions in the final solution is in the range of
- 10 0.001-0.3, more preferably of 0.005-0.15 g Cu/mL.
10. Method according to any of the preceding claims, wherein the amount of Cu ions in the final solution is such that a catalyst is obtained comprising 1-50 %wt, more preferably 10 to 30 %wt, and
- 15 most preferably 15 - 25 %wt Cu.
11. Method according to any of the preceding claims, wherein the concentration of ions of the complexing agent in the final solution is in the range of 0.001-1.5, more preferably of 0.15-0.5
- 20 g/mL.
12. Method according to any of the preceding claims, wherein the amount of ions of the complexing agent in the final solution is such that the molar ratio of metal to complexing agent is in the
- 25 range of 0.1 to 5, more preferably 0.5 to 2, and most preferably 0.75-1.25.
13. Method according to any of the preceding claims, wherein the concentration of ions of the at least one second metal in the
- 30 final solution is in the range of 0.001-0.3, preferably in the range of 0.005-0.15 g/mL.
14. Method according to any of the preceding claims, wherein the amount of ions of the at least one second metal in the final
- 35 solution is such that catalyst is obtained with an atomic ratio of Cu to the at least one second metal in the range of 0.01-10, more preferably in the range of 0.1-5, and most preferably in the range of 0.3-3.0.



15. Method according to any of the claims 7-14, wherein the concentration of ions of the at least one third metal in the final solution is in the range of 0.0001-0.03, preferably in the range of 0.0005-0.015 g/mL.
16. Method according to any of the claims 7-15, wherein the amount of the at least one third metal is such that catalyst is obtained with an atomic ratio of the at least one third metal to Cu in the range of 0.001-0.05, more preferably in the range of 0.001-0.01.
17. Method according to any of the preceding claims, comprising an additional step g) of pulverising the obtained catalyst.
18. Method according to any of the preceding claims, wherein the at least one second metal is chosen from one or more of Fe, Zn, Co, Ni, or a combination thereof.
19. Method according to any of the preceding claims, wherein the at least one third metal is chosen from one or more of Pd, Ru, Pt, Rh, or a combination of two or more thereof.
20. Method according to any of the preceding claims, wherein the inert carrier is chosen from alumina, silica, silica-alumina, titania, magnesia, zirconia, zinc oxide, or any combination thereof.
21. Method according to any of the preceding claims, wherein the inert carrier is present in an amount of 0-95 %wt, more preferably about 50-90 %wt, most preferably 70-85 %wt.
22. Chromium-free catalyst comprising Cu and at least one second metal obtainable by a method according to any of the preceding claims.
23. Chromium-free catalyst according to claim 22, said catalyst comprising at least 5 %wt Cu and having an atomic ratio of Cu to the at least one second metal of 0.1-10.

24. Chromium-free Cu-Zn catalyst supported on silica, zirconia, or magnesia according to any of claims 22 or 23, comprising 5-50 %wt, preferably 10-30 %wt (Cu + Zn) and having a Cu to Zn ratio of 0.1-10 at/at, preferably 0.5-5 at/at, more preferably 1-4 at/at.

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25. Chromium-free Cu-Zn catalyst according to claim 24, further comprising as at least one second metal Co or Ni, or a combination thereof.

10 26. Chromium-free Cu-Zn catalyst according to any of claims 24 or 25, further comprising at least one third metal chosen from Rh, Ru, Pd and Pt, or combinations of two or more thereof.

15 27. Chromium-free Cu-Zn catalyst according to claim 26 having a ratio of (Cu + Zn) to the at least one third metal of 0.0001-0.5 at/at, preferably of 0.001-0.01 at/at.

20 28. Chromium-free Cu-Fe catalyst supported on silica, zirconia, or magnesia according to any of claims 22 or 23, comprising 5-50 %wt, preferably 10-30 %wt (Cu + Fe) and having a Cu to Fe ratio of 0.1-10 at/at, preferably 0.5-5 at/at, more preferably 1-4 at/at.

25 29. Chromium-free Cu-Fe catalyst according to claim 28, further comprising as at least one second metal Co or Ni, or a combination thereof.

30 30. Chromium-free Cu-Fe catalyst according to any of claims 28 or 29, further comprising at least one third metal chosen from Rh, Ru, Pd and Pt, or combinations of two or more thereof.

30

31. Chromium-free Cu-Fe catalyst according to claim 30 having a ratio of (Cu + Fe) to the at least one third metal of 0.0001-0.5 at/at, preferably of 0.001-0.01 at/at.

35

32. Use of chromium-free catalyst according to any of claims 22-31 for the hydrogenation of fatty acids, fatty esters, esters and diesters to fatty alcohols, alcohols and dialcohols, respectively.